DEVELOPMENT AND CHARACTERIZATION OF

PELLET ACTIVATED CARBON FROM NEW PRECURSOR

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CERTIFICATE

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NOMENCLATURE

BET	: Brunauer Emmett Teller
IUPAC	: International Union of Pure and Applied Chemistry
PAC	: Powdered Activated Carbon
GAC	: Granular Activated Carbon
EAC	: Extruded Activated Carbon
SEM	: Scanning Electron Microscope
FTIR	: Fourier Transform Infra-Red Spectroscopy
HVAC	: Heating, Ventilation and Air Conditioning
°C	: Degree Celsius
cm/g	: centimetre per gram
HCl	: Hydrochloric Acid
mg/g	: milligram per gram
KOH	: Potassium Hydroxide
H_3PO_4	: Phosphoric Acid
CO_2	: Carbon-di-oxide
AC	: Activated Carbon
$ZnCl_2$	: Zinc Chloride
w/w	: weight by weight ratio
mL/min	: millilitre per minute
Hg0	: Elemental Mercury
PAN	: Polyacrylonitrile
NaOH	: Sodium Hydroxide
K	: Kelvin
TGA	: Thermogravimetric Analysis
CHNS	: Carbon, Hydrogen, Nitrogen and Sulphur
TCD	: Thermal conductivity detector
IR	: Infra-Red

ABSTRACT

Coconut shell was used as a precursor for the production of activated carbon. The substrate was initially physically activated for determination of optimum temperature of production. However on comparison with various chemical activations, zinc chloride activation produced the best results. Preliminary tests determine the inefficiency of epoxy resins as binders. Later concentrated sugarcane juice was used as an adhesive for pellet formation. On activation of these pellets, enhanced surface properties (better than powder activated carbon using same procedures) are obtained. The characteristics of the pellet activated carbon were studied through various tests and analysis. The iodine number of the pellet activated carbon was determined to be 1100 mg/g and had a yield of 36.95%. However the powder activated carbon had an iodine number of only 1020 mg/g. The adsorption study of the pellet activated carbon hence provides evidence for better activity and surface area than commercial activated carbon. It also determines a suitable application of Methane gas storage by adsorption on this pellet activated carbon at high pressure.

Chapter 1

Introduction

1. INTRODUCTION

1.1 Activated Carbon

Activated carbon is a form of carbon species that is processed and prepared to have high porosity and very large surface area available for adsorption.

Activated carbons are sometimes called as active carbons due to their highly developed internal surface area and porosity. The large surface area implies a high capacity for adsorbing chemicals from gases and liquids. The most widely used commercial active carbons have a specific surface area varying from 800 to1500 m^2/g, as determined typically by nitrogen gas adsorption (BET surface area) [1]. Difference in pore size affects the adsorption capacity for molecules of different shapes and sizes, and thus is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes. They are:

Micropores: width less than 2 nm

Mesopores: width between 2 nm and 50 nm

Macropores: width greater than 50 nm

1.2 Preparation of Activated Carbon

Activated carbon is generally produced from carbonaceous materials or in general biomass substances like nutshells, peat, wood bagasse, lignite and coal. It can be produced by one of the following processes.

1.2.1 Physical activation

The precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the following processes:

• *Carbonization*: Material with carbon content (the biomass precursor) is pyrolyzed at high temperatures, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)

• *Activation/Oxidation*: Raw material (precursor) or carbonized material (product obtained from carbonization) is exposed to oxidizing agents (carbon dioxide, oxygen, or steam) at high pressure and temperature [1].

1.2.2 Chemical activation

The raw material is impregnated with certain chemicals at specific ratios before carbonization. The chemical is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, etc.). Then, the impregnated raw material is carbonized at lower temperatures (comparatively lower than physical carbonization). It is believed that the carbonization and activation occurs simultaneously during chemical activation. Chemical activation is preferred over physical activation because it requires lower temperatures and shorter time for activating the material [1] [2].

1.3 Types of Activated Carbon

Classification is done based upon their surface characteristics, behavior and preparation methods.

1.3.1 Powdered Activated Carbon (PAC)

Powdered Activated Carbon is fine granules whose size is less than 1.00 mm. Their average pore diameter is between 0.15 to 0.25 mm. They are usually prepared by finely ground raw material. PAC is not generally used because of their high pressure loss in applications. However, their main property is the presence of a high surface area to volume ratio.

1.3.2 Granular Activated Carbon (GAC)

Granular Activated Carbon is comparatively larger in size than Powdered Activated Carbon. This type of activated carbon exhibits a lower surface area than PAC. GAC is used for deodorization, water treatment and separation of components in a flow system and can also be used for gas/vapor phase applications.

1.3.3 Extruded activated carbon (EAC)

Extruded Activated Carbon is cylindrical shaped activated carbon with diameters ranging from 0.8 to 130 mm. Since they are of bigger size they have high mechanical strength, low dust content and low pressure drop during application. Hence they are used for gas phase applications.

1.3.4 Impregnated carbons

Inorganic metals like aluminum, manganese, zinc iron, lithium and calcium are impregnated upon them for specific applications related to air pollution control. This type of activated carbon also finds usage in water purification processes when impregnated with specific kinds of antimicrobial/antiseptic agents.

1.3.5 Polymers coated carbon

It is a process of preparing biocompatible polymer to give a smooth and permeable coat without blocking the pores. It is used as an absorbent in hemoperfusion and other medical related adsorption operations.

1.4 Pellet Activated Carbon

Pellet Activated Carbon is generally used where high pressure operations and high volumetric adsorption is required. As the name suggests, these activated structures are compact, hard and have a very high surface area for adsorption. Usually pellet activated carbons have a length of 20 mm to 40 mm and a diameter of 5 to 10 mm.

The main reason to use a pellet for adsorption is because of its unique pore distribution. The mesoporosity of these pellets are highly enhanced and hence have a great effect in gas adsorption processes. However, due to certain fluctuations in production, these pellets can also be used for liquid adsorption purposes too [3]. The main application and function of an activated carbon is determined by its characteristic studies like BET surface area, SEM, FTIR, Iodine Number, Carbon Tetrachloride Number, etc.

The major applications of Pellet Activated Carbon are [3]:

1. Solvent Recovery
2. Gas purification and processing
3. Volatile Organic Compounds Control
4. Catalyst Support
5. HVAC (Heating, Ventilation and Air Conditioning)

Chapter 2

Literature Review

2. LITERATURE REVIEW

The following are the different raw materials that have been used for the production of activated carbon in the journals mentioned below.

Table 1 List of raw materials which have been used for the production of activated carbon.

Raw Material	References
Gelam wood bark	Abdul Halim Abdullah , Malaysian Journal of Analytical Sciences [4].
Coconut shell	J. Laine , Carbon [5].
Agricultural residues and bagasse	Javier Blanco Castro, Ind. Eng. Chem. Res. [6].
Physic nut	Viboon Sricharoenchaikul, Energy and Fuels [7].
Natural biomaterial bamboo	A.W.M. Ip, Bioresource Technology [8].
Vetiver roots and sugarcane bagasse	N. Passe-Coutrin, Microporous and Mesoporous Materials [9].
Bagasse and rice husk	Dimitrios Kalderis, Bioresource Technology [10].
Spanish bituminous coal	Francisco Carrasco-Marin, Fuel [11].
Oil-palm stone	Jia Guo, Microporous and Mesoporous Materials [12].
Polyethyleneterephthalate (PET)	M.T. Kartel, Carbon [13].
Eucalyptus camaldulensis Dehn bark	Phussadee Patnukao,Bioresource Technology[14].
Marine macro-algal biomass Sargassum longifolium and Hypnea valentiae	R. Aravindhan, Journal of Hazardous Materials [15].
Luscar char	R. Azargohar, Microporous and Mesoporous Materials [16].
Corn Cob	W.T. Tsai, Bioresource Technology [17].
Waste tires	P. Ariyadejwanich, Carbon [18].
Neem husk	Alau K. K, Archives of Applied Science Research [19].
Carbon black and polymer binder	Zhongren Yue, Microporous and Mesoporous Materials [20].

Rubber separated from waste tires was carbonized at 500 °C in nitrogen atmosphere. The obtained charcoal was activated with steam at 850 °C. The mesoporous activated carbons had mesopore volumes and BET surface areas up to 1.09 cm /g and 737 m^2 / g, respectively. For improving the properties the porous properties of the activated carbons, the char was treated with 1 M HCl prior to steam activation. This treatment increased the mesopore volumes and BET surface areas of the activated carbons up to 1.62 cm /g and 1119 m^2/ g, respectively [18].

Coconut shell is suitable for preparing microporous activated carbon due to its excellent natural structure and low ash content. Activated carbon can be produced by chemical activation or physical activation.

Manufacture of microporous activated carbon from raw coconut shell was done by a two-step procedure. During the process, the raw coconut shell was first heated in an inert environment to temperatures between 450 °C and 850 °C, and reacted with oxygen. It was heated again in inert environment to an activation temperature (850 °C) to produce activated carbon. Activated carbons with specific surface area greater than 700 m^2/g were manufactured. It also had a yield between 24% and 28%. It was shown that the carbon had a narrow distribution of pore size [21].

Physic nut was used as a raw material. The raw material is pyrolyzed at 400-800°C withhold times of 15, 120,240 minutes to obtained char precursor. Activated carbon, with favorable BET surface area in a narrow range, was prepared by soaking these chars in concentrated KOH, H_3PO_4, as well as a pure CO_2 gas flash activator. The maximum specific surface area of 532.30 m^2 g-1 was developed for the alkaline-treated sample. According to the data

obtained, physic nut residue pyrolyzed at 800°C and followed by KOH activation could be used as a low-cost adsorbent with favourable surface properties [7].

Physical activation with pure CO_2 at 800 °C resulted in a bimodal pore size distribution featuring both the widest macropores and the narrowest micropores among the samples studied. The introduction of potassium phosphate as a catalyst for the gasification with CO_2 led to a decrease in macropore volume and diameter, and to a slight increase in micropore diameter. Surface area was found to increase with increasing micropore diameter. Wider micropores and significant mesoporosity resulted when employing chemical activation with phosphoric acid at a lower temperature (500°C) [22].

Commercial activated carbon is a preferred adsorbent for the removal of micro pollutants from the aqueous phase. Research and experiments are done to find inexpensive alternative activated carbon (AC) precursors, such as waste materials. It is evident that conventional (from agriculture and wood industry) and nonconventional (from municipal and industrial activities) wastes can be used to prepare AC, which are applied in treatment processes, namely to remove organic pollutants, dyes, volatile organic compounds, and heavy metals from water and other liquid medium. Moreover, high surface areas can be obtained using either physical or chemical activation. But combined treatments might enhance the surface properties of the activated carbon having higher adsorption capacity [23].

Gelam wood bark was used as a precursor to prepare the activated carbon .The preparation process consisted of $ZnCl_2$ impregnation followed by carbonization in nitrogen at 500^oC for 3 hours and carbon dioxide for 1 hour. The optimum surface area was obtained at 25 % of $ZnCl_2$, which is 1213 and 1443 m^2/g for BET and Langmuir, respectively [4]**.**

One step carbonization process was used to prepare activated carbon by coconut shell as precursor impregnated with phosphoric acid .The optimum activation temperature obtained for higher surface area 1180 m^2/g was 450^oC [5].

Activated carbons were prepared from two different types of sugar cane wastes, agricultural residues and bagasse. The precursor are impregnated by phosphoric acid activation varying the carbonization temperature (300^oC - 600°C), the weight ratio of phosphoric acid to precursor (R = 1-2.5), and carbonization time (0-3 hours). Bagasse carbons showed higher surface area and pore volume than those from agricultural residues. Maximum surface areas of around 1100 and 780 m^2/g were respectively attained. Iodine number between 608 and 746 and methylene blue uptake of 213-261 (mg/g) were determined for the selected samples [6].

With an objective of storing natural gas, chemical activation with phosphoric acid was used for the preparation of activated carbon samples from coconut shells. Some variations in the activation scheme were introduced, such as pre-treatment with acid and carbonization under inert atmosphere (nitrogen). This result suggests that activated carbons prepared from "Coco da Baía" by chemical activation with phosphoric acid have potential to be used as a storage media for natural gas storage [24].

The samples were dried at 100 °C for 2 hours. Impregnation was carried out at 85 °C with phosphoric acid solutions at increasing concentrations (53% w/w). The ratio between raw material and phosphoric acid was 1:2. After impregnation, the samples were carbonized. The carbonization process was carried out under nitrogen flow (500 mL/min). After carbonization, the samples were washed with distilled water to thoroughly remove the remaining phosphoric acid [24].

The effect of the preparation conditions on the yield activated Neem husk prepared by using $ZnCl_2$, H_3PO_4 and KOH as activating agents was studied. The raw Neem husk was processed

and carbonized at 400 °C and its corresponding yield was 63.6%. The optimum conditions for the activated carbon production was evaluated based on the determination of various adsorption parameters [19].

The adsorption studies show that the activation was actually successful when compared to the carbonized Neem husk that was not activated [19].

At initial concentration of 5ppm, it is observed that the Neem carbon activated with $ZnCl_2$ adsorbed 96.69% of the methylene blue and these competed very well with the commercial activated carbon from coconut which has 97.29% while KOH and H_3PO_4 activated samples had lower values [19].

The effects of temperature, time and impregnation ratio on activation of coconut shell and its yield were studied. Experimental results show that higher temperature produces better activation but lower yield [25].

The activation agent influences the pyrolytic processes so that the formation of tar is restricted to a minimum and the amount of aqueous phase in the distillate is also less than in normal carbonization.

The impregnated charcoal was dried at 120 °C and placed in a muffle furnace at a pre-selected temperature and time. An inert atmosphere was maintained throughout the operation by supplying nitrogen into the furnace. At the end of activation time, the samples were washed with water, dried at 120 °C and stored for analysis.

Chemical activation produces highly active carbon, which presents a wider, meso- and macro-porosity.

Coconut shell carbons have several advantages like high density, high purity. They are virtually dust-free, since they are harder and more resistant to attrition. There is a uniform

pore structure distribution, with the majority of pores having size in the microporous range [25].

Hg0 adsorption experiments with different kinds of activated carbons (ACs) were conducted in nitrogen environment to study the effects of ACs with different surface characteristics on adsorption. ACs prepared by steam activation did not adsorb elemental mercury (Hg0) in nitrogen environment, while another kind of AC prepared by chemical activation using zinc chloride ($ZnCl_2$) showed significant Hg0 adsorption capability because Hg0 was oxidized by the oxidative elements on the surface of AC [26].

Microporous activated carbon samples were prepared from coconut shells, using chemical activation with zinc chloride impregnation and then physical activation. The sample was then evaluated for methane adsorption. These results suggest that activated carbons prepared from coconut shells, using chemical activation followed by physical activation, are suitable adsorbents for natural gas storage applications [27].

High surface area, highly mesoporous carbon granules in the form of pellets were prepared by first mixing a solution of polymer (phenolic resin, cellulose, or PAN) with water and a chemical reagent (NaOH or ZnCl2). Chemical activation increases the BET surface area as well as the microporous and mesoporous volumes of the resulting carbon pellets [28].

Carbon black powder was then added to form a mixture, which was later moulded into a pellet. Then the pellet was dried and activated at a given temperature. The pore structures of the porous carbon binder and the resulting carbon pellets were characterized using N_2 adsorption/desorption at 77 K and SEM [28].

Activated Carbon can be produced from any carbonaceous material such as wood, lignite, anthracite, bone etc. A high quality gas adsorption grade activated carbon can be produced

from coconut shell a waste product. Activated carbon may be of different form such as powdered, granular or pelletised material. For gas separation and purification processes, regular shaped pellets are preferable to Irregular granular material due to a lower fluid pressure drop [29].

Production of activated carbon was carried out by the following steps:

i) Coconut shell particles were carbonized by destructive distillation in a furnace at 550 °C for one hour for completion of the carbonization process.

ii) Powdered char was then mixed with phenol-formaldehyde resin as the binder. The proportionate weight of binder and char was adjusted in such as a way so as to give reasonable strength in the finished pellets. The pellets were produced from the char resin mixture in a pelletizer machine by application of pressure.

iii) These carbon pellets were then treated in an activating furnace and steam at a pressure of 1.5 bar was passed through it at a temperature of 750 °C for 2.0 hour to produce the ACP-750-2.0, grade activated carbon pellets [29].

The lack of information in the literature and also the varied application interest of Pellet Activated Carbon made it a reason for examination and to check the feasibility in the present work. Hence the main objective was to prepare, develop and characterize pellet activated carbon from coconut shell powder as a precursor using sugarcane juice as a binder.

Chapter 3

Materials and Methods

3. MATERIALS AND METHODS

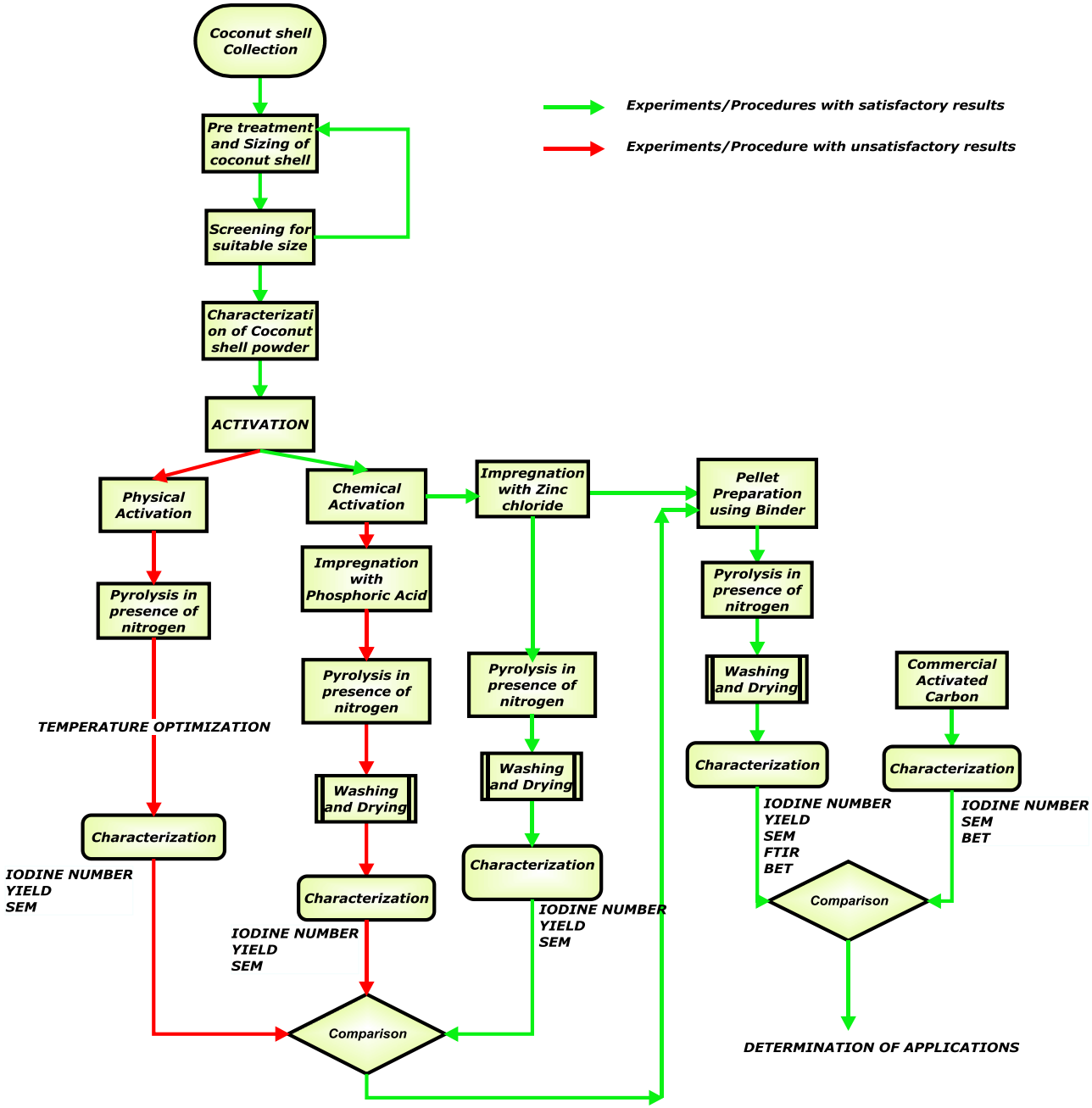

Fig. 1. Methodology of the project.

3.1 Chemicals

A lot of chemical has been used throughout the project. All the chemicals that were used in the lab were bought from Adarsh Enterprisers, Rourkela. Chemicals used for the project were pelletized iodine , potassium iodide, starch, sodium thiosulphate, hydrochloric acid, zinc chloride, potassium hydroxide, phosphoric acid, epoxy resin, binderetc. Methane gas cylinder was procured from S.K.P Corporation located in Rourkela.

3.2 Instrumentation

A shaker (Lab Companion model SI-300R) was used for all the adsorption experiments. Fourier transform infrared spectrometry (Perkin Elmer, revolution of 4 cm^{-1}) was used to analyze the organic functional groups present in the adsorbent. Scanning electron microscope (SEM - JEOL, JSM 6480 LV) was used to know the surface texture and porosity of the sample. CHNS analyzer (Elemental CHNS analyzer) was used to estimate ultimate analysis of the sample. Tubular furnace (Bysakh, maximum temperature 1200 °C) was used to prepare the activated carbon. Thermograviametric analyser (Schimadzu, DTG - 60H) helped to determine the weight loss with temperature increase. Specific surface area and porosity was estimated using BET surface area analyzer (Autosorb, Blue star Ltd.).

3.3 Biomass Raw Material

Coconut shells were collected from Sri Ayyappa Swami Seva Samaj, (Ayyappan Temple) Rourkela. It was then pretreated before activated carbon was produced.

3.4 Pretreatment of Raw Material

Coconut shells were dried in the sun for 6 to 8 hours. Later the dried shells were crushed using a hand crusher to very fine powder. The crushed powder was then sieved and only the powder was selected as precursor for the production of activated carbon. It is then exposed to

various environment conditions to produce Activated Carbon by physical method. The precursor is initially characterized using TGA, Proximate Analysis, Ultimate Analysis and FTIR.

3.5 Thermo gravimetric Analysis

Thermo Gravimetric Analysis of a substance implies the degradation of weight with respect to time and temperature. The advantage of TGA is that the weight loss at given time or temperature can be evaluated. This serves as a basic study for the activation process. It is this process which helps to determine the range of working temperatures to work on.

For the Thermo Gravimetric Analysis to be carried out, small amount of the sample (20 mg) was placed in a vial, which was present in the TGA analyzer. This vial is connected to sensors which detects the weight of the sample at all times. The test needed certain values like, the rate of heating in °C/min, the maximum temperature to which the sample was heated and the retention time of the sample at the maximum temperature. These values were used as basis for the analysis.

3.6 Proximate Analysis

The proximate analysis of coal is used to determine the distribution of products obtained when the coal sample is heated under specific conditions. It is defined by ASTM D 121; and separates the products into four groups:

(1) *Moisture*: water content present in the sample

(2) *Volatile matter*: gases and vapors driven off from the sample during the heating process

(3) *Fixed carbon*: nonvolatile fraction of sample (basically the carbon content of the sample)

(4) *Ash*: inorganic residue remaining after combustion (inert matter present in the sample)

To determine the four products on heating, the sample is subjected to specific conditions for each test.

3.6.1 Moisture Content

According to this test the sample was heated in a petri dish at 105°C for 1hour 30 minutes in an oven. The weight of the sample before heating and after heating was determined. This specifies the amount of moisture content present in the sample.

3.6.2 Volatile Matter Content

The procedure implies that the sample was heated at 925 °C ± 25°C in a closed crucible for 7 minutes 30 seconds. The heating was done in a muffle furnace. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. Larger weight loss of the substance implies greater volatile matter content.

3.6.3 Ash Content

To determine the ash content, the sample was heated at 725 °C ± 25°C in an open crucible for 1 hour 30 minutes in a furnace. The weight of the sample before heating and after heating was used to determine the amount of ash content present in the sample. In this test, the amount of residual substance is equal to the ash present in the sample.

3.6.4 Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The value obtained is the amount of fixed carbon present in the sample expressed in percentage.

Fig. 2. Hot Air Oven used for heating and drying.

3.7 Ultimate Analysis (CHNS)

The Ultimate Analysis of a sample determines the elemental composition of the sample. It is based on the principle of Dumas method which involves the complete and instantaneous oxidation of the sample by flash combustion. The results are in percentage composition of Carbon, Hydrogen, Nitrogen and Sulphur. From these results the oxygen composition is determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100.

The Ultimate Analysis was carried out in a CHNS Analyzer. The sample is fed into the analyzer along with excess supply of oxygen. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulphur) present in the sample produces carbon dioxide, water, nitrogen dioxide, and sulphur dioxide respectively. The combustion products are separated by a chromatographic column and are detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample.

3.8 Preparation of Activated Carbon

Various ingredients and medium can be used for the preparation of activated carbon. To develop high activated surfaces on the coconut shell powder, the following two methods of activation were used.

3.8.1 Physical activation

To determine the optimum temperature for activation, the powdered coconut shell was subjected to various temperatures. Activated carbon was produced at different temperatures (temperature range determined from TGA of precursor). The weighed sample was kept in the tubular furnace and heated to the final temperature at a rate of 4°C/min. A retention time of 1 hour was kept for all the activated samples produced. The whole process was carried in an inert medium of nitrogen. A flow of 500 ml/min of Nitrogen was allowed through the tubular reactor for activation of coconut shells. The sample in the reactor was cooled to room

temperature in the Nitrogen flow. The cooled samples were then weighed and collected in air tight bags.

Activation of the precursor was carried out by subjecting the carbonized coconut shell powder to high pressurized steam in an autoclave. The activation was carried out using 3 bar ± 0.5 bar pressure for 2 hours. The activated sample was then dried in an oven at 105 °C for 3 hours. The dry activated samples were then stored in air tight bags.

Fig. 3. Tubular Furnace used for pyrolysis.

3.8.2 Chemical activation

Chemical activation was carried out using three different chemicals, namely potassium hydroxide, phosphoric acid and zinc chloride. Impregnation ratio is defined as the ratio of amount of chemical used for impregnation (in g) to the amount of precursor (biomass sample) (in g) used. All the three chemicals used had a concentration of 50% w/w. The powdered coconut shell powder was initially impregnated with each of the sample in separate conical flasks. The samples were left impregnated for 14 hours at 85 °C in an oven. The impregnation ratios used are depicted in Table 2.

Table 2 Impregnation Ratio of various activating agents used for chemical activation.

Chemical Used	Impregnation Ratio
Phosphoric Acid	2:1
Zinc Chloride	1:1
Potassium Hydroxide	3:1

This caused all the excess liquid to evaporate and only dry impregnated sample was left over in the conical flask. The dry samples were then weighed and kept in the tubular furnace and heated to 550 °C at a rate of 4°C/min. A retention time of 1 hour was kept for all the activated samples produced. The whole process was carried in an inert medium of nitrogen. A flow of 500 ml/min of Nitrogen was allowed through the tubular reactor for chemical activation of coconut shells. The sample in the reactor was cooled to room temperature in the Nitrogen flow. The cooled samples were then washed and dried. The dried activated carbon were then weighed and collected in air tight bags.

3.8.3 Pellet Formation

The chemically impregnated coconut shell were finely ground using a hand grinder. The ground precursor was then kept in the oven at 105 °C for 1 hour to make it moisture free.

This sample was then mixed with the binder and epoxy resin which formed a gluey and viscous adhesive. The ratio of the binder to epoxy resin used was 1:9. This mixture was thoroughly mixed and made into dough. The dough was then rolled into cylindrical pellets by hand. These pellets were then activated according to the procedure described in 3.7.2.

The chemically impregnated sample was mixed with concentrated sugarcane juice and was made into dough. While making the dough, few drops of water was also added to the mixture to make it smooth. The dough was then shaped into uniform cylindrical pellets using a pelletizer gun. The dough was filled into the gun, and then was pressed from the top. This eventually pushes out the pellets. These pellets were then dried in the oven at 105 °C for 6 hours. On drying the pellets had a very stable and rigid structure.

3.9 Iodine Number

Iodine number is the mass (mg) of iodine adsorbed from a standard 0.1 N (0.05 M) iodine solutions, when the equilibrium iodine concentration is exactly 0.02 N (0.01 M). The iodine number is a relative indicator of porosity in activated carbons. For high surface area carbons (greater than 900 m^2/g), iodine number is numerically similar to BET surface area measurements, whereas for low surface area active carbons, this one-to-one correlation of surface area with iodine number falls away.

According to the procedure defined by ASTM D4607 - 94(2006), for determination of iodine number 0.7- 2 g of activated carbon was added with 10ml of 5% HCl and swirled in a conical flask until the entire activated carbon was wetted. The wetted solution was then boiled for exactly 30 seconds and the solution was cooled to room temperature. Then 100ml of 0.1N iodine solution was added to the contents of the conical flask. This solution was filtered using a Whatman 2V filter paper. Later 50ml of this filtrate was then titrated against sodium thiosulphate in the presence of starch as indicator. The equilibrium concentration is determined by calculation using the amount of sodium thiosulphate used in the titration. If this equilibrium concentration was not within the range of 0.008 to 0.334, then the procedure was repeated with a different amount of activated carbon. This was a trial and error method, and terminates only when the equilibrium concentration lies within that range.

3.10 Fourier Transform Infrared Spectroscopy

The infrared spectrum is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals the amount of energy that was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced. These spectrums detect the IR wavelengths at which absorption occurs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular

structures lead to more absorption bands and more complex spectra. The technique has been used for characterization of various mixtures [30] [31].

3.11 Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

Small amounts of the sample were initially placed on a circular disc like structure, which is the base for the analysis. This base can be moved automatically. The samples were attached to the surface of the disc using specific tapes. The whole disc with the samples was placed in the electron chamber, where the electron gun sprays a beam of electron for scanning. The electrons interacting with the atoms produced images of the surface topography, which was viewed on a monitor. The magnification of the scan was varied for a better quality image and proper clarity of the surface. The images of specific magnifications were saved. The SEM images clearly depict the pores and nature of the surfaces of activated carbon.

3.12 Adsorption Studies

The volumetric apparatus was kept immersed in a constant temperature water bath maintained at uniform temperature. The adsorbed volume was determined at constant temperatures as a function of pressure at equilibrium. Equilibrium at each isotherm point is

assumed to have been reached at a constant pressure after 8 hours. Real gas law was applied to determine the gas adsorbed. Peng-Robinson Equation of State was used to calculate the compressibility factor in the real gas equation. The fixed volume and the void volume were determined through helium expansion. Correction for the gas adsorbed at each isotherm step was accomplished assuming the liquid density of the adsorptive. After conducting the experiment at a fixed temperature, the sample was depressurized. The temperature of the water bath was maintained at the fixed temperature and the process was repeated for adsorption study with the new samples.

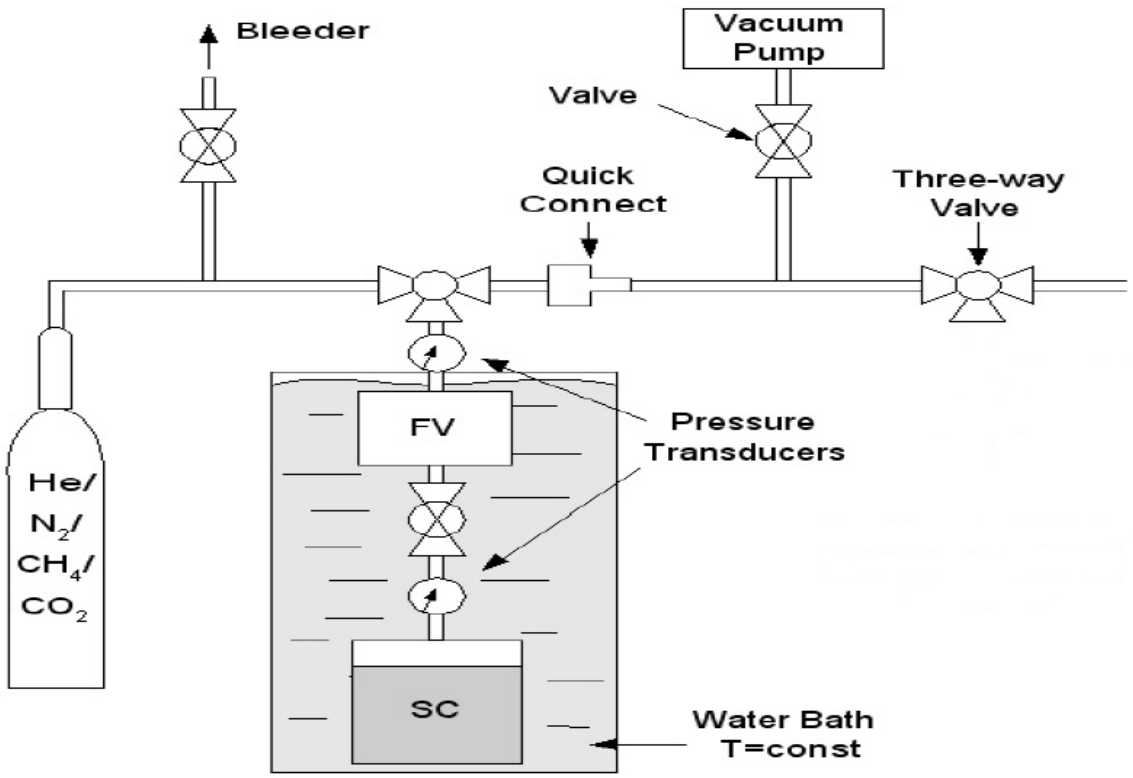

Fig. 4. Line diagram of fabricated setup.

Chapter 4

Results and Discussion

4. RESULTS AND DISCUSSION

4.1 Thermogravimetric Analysis

The TGA result of coconut shell powder clearly indicates that the initial weight loss begins at a temperature around 100°C. But the drastic change in weight is felt only when the temperature reaches around 300°C. Henceforth there is a steep and steady weight loss of powdered coconut shell. It can also be noted that the maximum loss of weight is achieved at a temperature of about 650°C. The constant line towards end of the TGA graph implies a constant ash that is left over. The quality of activated carbon depends on the process and technique of removal of volatiles from the sample. It also varies with the rate of dehydration of the sample. Hence taking these into consideration, it can be identified that there is maximum loss of weight in the temperature range of 500°C to 650°C.

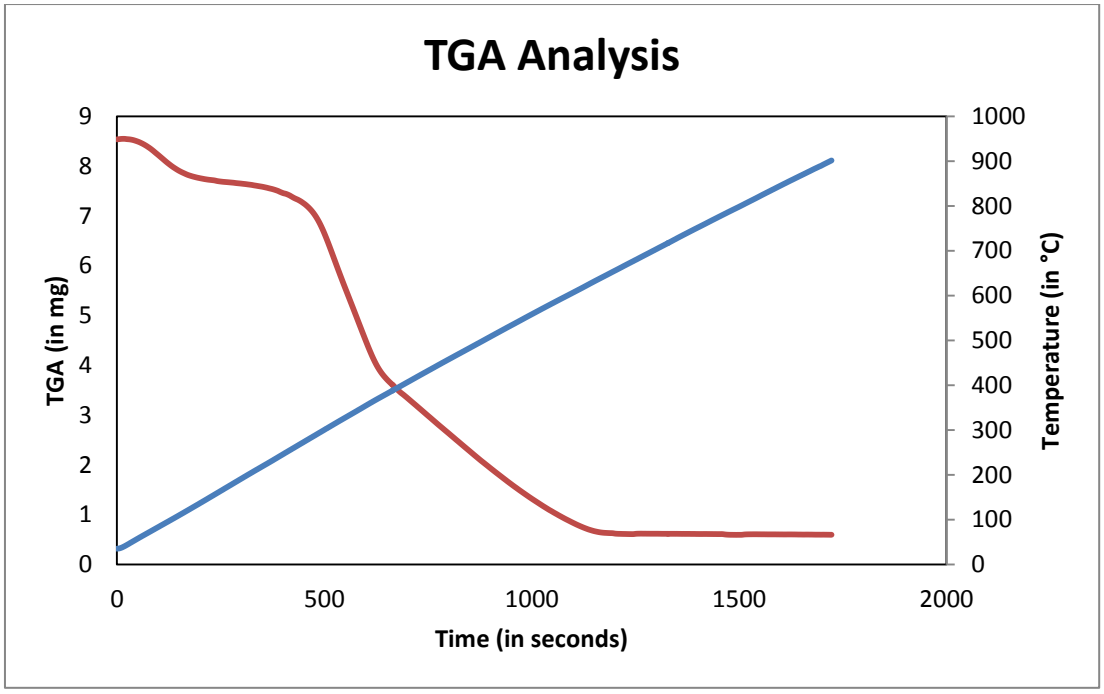

Fig. 5. TGA thermograph of coconut shell.

4.2 Proximate Analysis

The Proximate Analysis result of coconut shell determines the distribution of its contents. It may be noted that the volatile matter present in coconut shells, contributes maximum to its contents. The moisture content present in the sample can also be considered as water vapor when it is heated to high temperatures. Hence, about 73% of the contents tend to leave the sample when heated, of which 63.48 % is volatile matter and 9.78% is moisture content. The values from the table 3, indicates that the ash content of the sample is 15.55% and also fixed carbon content of the sample is 11.18%. This gives an overview about the properties and components of the precursor.

Table 3 Proximate Analysis of Coconut Shell.

Precursor Content	Composition
Ash Content	15.5520 %
Moisture Content	9.7804 %
Volatile Matter	63.4799 %
Fixed Carbon	11.1877 %

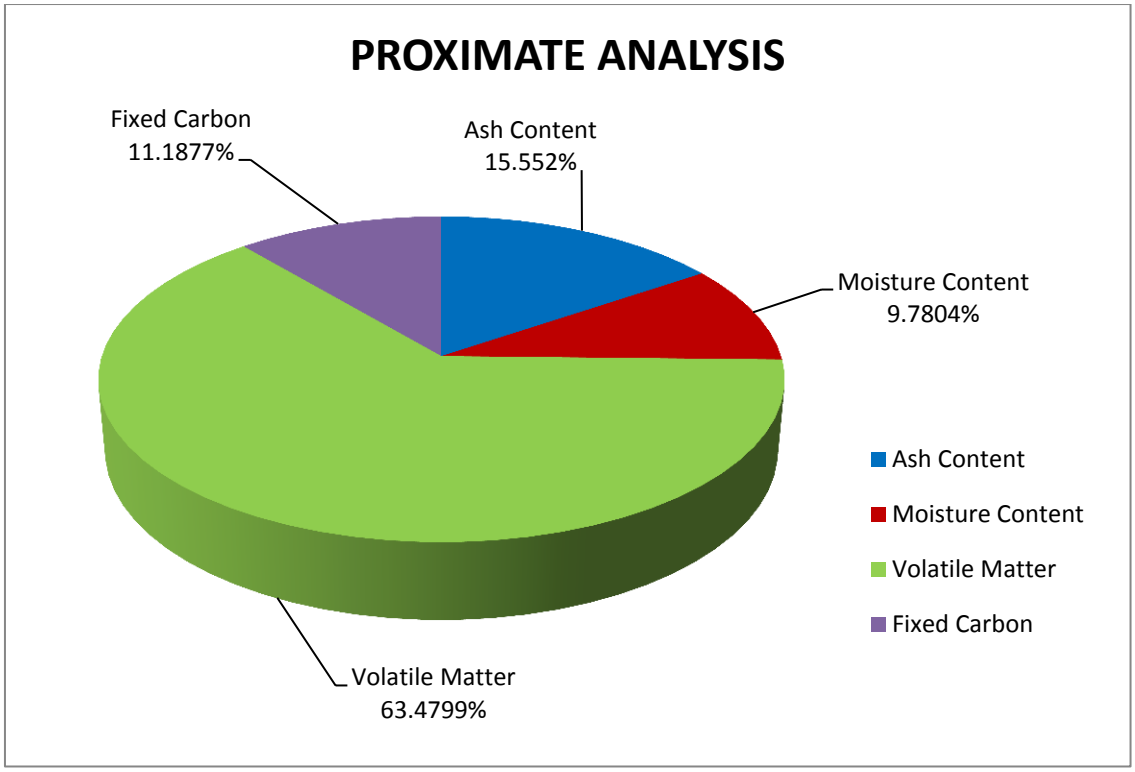

Fig. 6. Proximate Analysis of coconut shell.

4.3 Physical Activation for Temperature Optimization

The production of Activated was done at different temperature to determine an optimum temperature for highly active carbon.

4.3.1 Yield Percentage

It is the ratio of amount of activated carbon produced (in g) to the amount of precursor sample taken for activation (in g). This ratio gives an idea about the amount of content that has left the substrate during production of the sample. However, it might be a sole criterion for characterizing activated carbon.

Figure 7 depicts the yield% obtained at different temperatures.

Table 4 Yield Percentage of activated carbon produced at various temperatures by physical activation.

Activation Temperature (in ° C)	Yield (in %)
520	8.9520
540	28.9637
550	32.8248
560	29.1227
580	27.7742
600	27.8963
620	24.3723

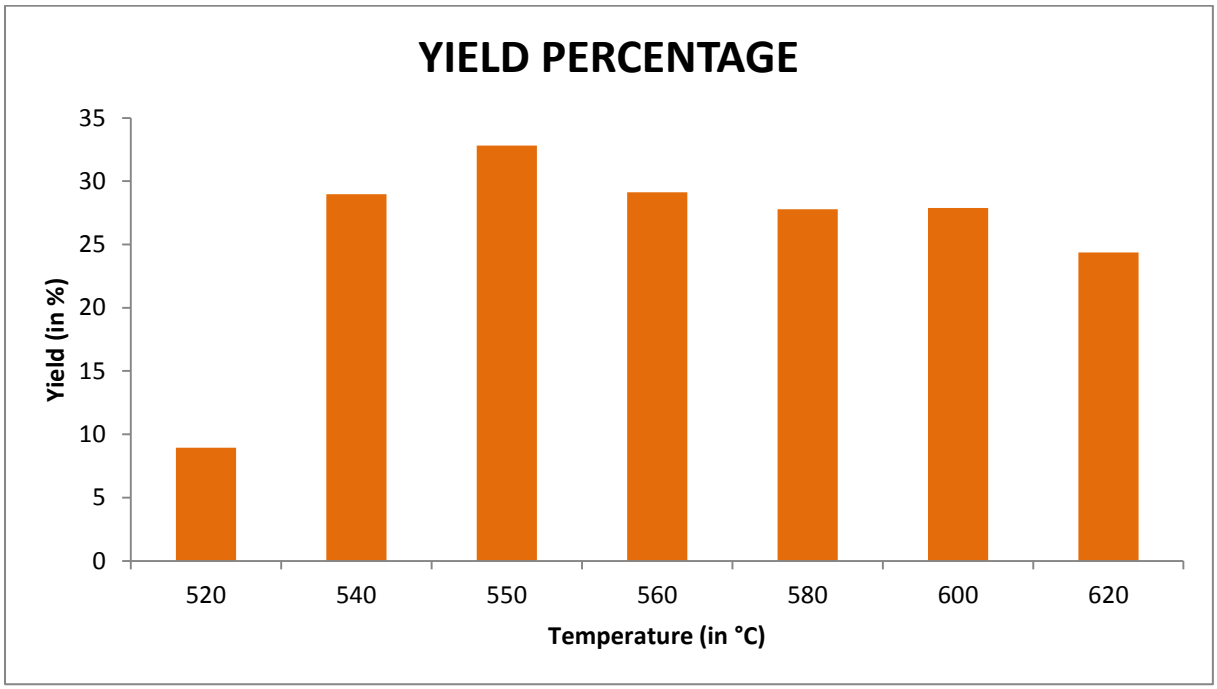

Fig. 7. Yield Percentage of activated carbon produced at various temperatures by physical activation.

4.3.2 Iodine number

The iodine number of activated carbon was used as a criterion for determining the activity of the product. It gives a better estimate of the amount of active surface present on the activated carbon. According to the ASTM procedures, the tests were done and the following results were obtained for activated carbon prepared by physical activation.

Table 5 Iodine Number of activated carbon produced at various temperatures by physical activation.

Temperature (in °C)	520	540	550	560	580	600	620
Iodine Number (in mg/g)	102.364	108.763	119.390	112.510	108.156	102.315	98.648

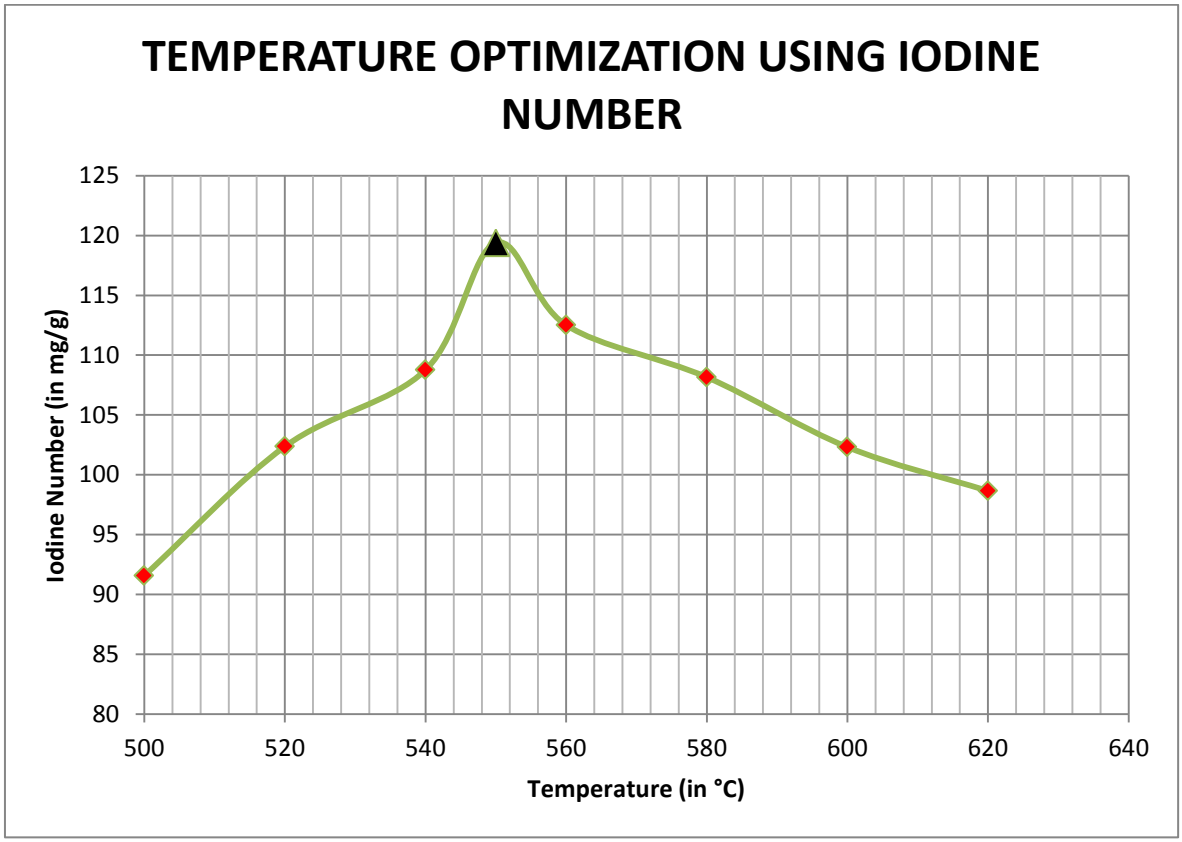

Fig. 8. Iodine Number of activated carbon produced at various temperatures by physical activation.

From figure 8, it is clear that the highly activated carbon was produced at a temperature of 550 °C. The activity of the products are determined as amount of iodine adsorbed in mg/g of the activated carbon. Greater the value of the iodine number, greater is the activity of the sample. Hence the optimum temperature for the production of activated carbon, by physical activation was determined to be 550 °C.

4.4 Chemical Activation

Due to low activity of product, physical method of activation was dropped and chemical activation had to be used. The chemical activation was carried out using phosphoric acid, zinc chloride and potassium hydroxide.

4.4.1 Yield Percentage

The yield percentage result of chemical activation using various chemicals is denoted in table 6. From figure 9, it can be clearly noted that the yield of zinc chloride activated sample is 44.7% while that of phosphoric acid activated sample is 52.84%. It is clearly evident that yield percentage is not the only sole criterion for optimization of activated carbon production.

Table 6 Yield Percentage of activated carbon produced using various activating agents by chemical activation.

Chemical Used for Activation	Impregnation Ratio	Yield (in %)
Powder Activated Carbon using Phosphoric Acid (H_3PO_4)	2:1	52.8455
Powder Activated Carbon using Zinc Chloride ($ZnCl_2$)	1:1	44.7070
Powder Activated Carbon using Potassium Hydroxide (KOH)	3:1	32.7692

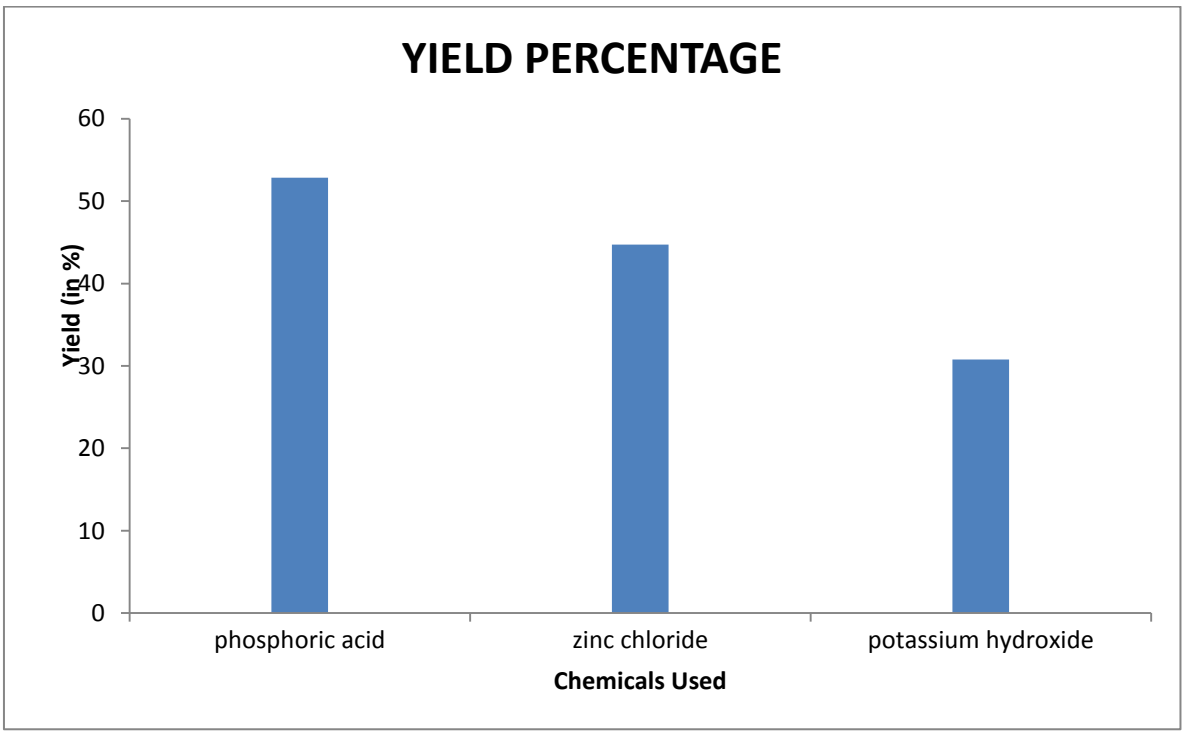

Fig. 9. Yield Percentage of activated carbon produced using various activating agents by chemical activation.

4.4.2 Iodine Number

Table 7 Iodine Number of activated carbon produced using various activating agents by chemical activation.

Chemical Used for Activation	Impregnation Ratio	Iodine Number (in mg/g)
Powder Activated Carbon using Phosphoric Acid (H_3PO_4)	2:1	693.8
Powder Activated Carbon using Zinc Chloride ($ZnCl_2$)	1:1	1021.8
Powder Activated Carbon using Potassium Hydroxide (KOH)	3:1	776.3

From Table 7, it is inferred that the activated carbon produced chemically using zinc chloride has the highest iodine number of 1021.8 mg/g. This indicates highly active surfaces present on the activated carbon, with high porosity and surface area. Meanwhile, the iodine number of other two products are not absolutely less, but comparatively lesser. Hence zinc chloride activation is considered efficient than the other two methods for the production of activated carbon from coconut shell.

4.5 Pellet Preparation and Activation

Pellets were formed using the binder and epoxy resin as adhesive. Figure 10, depicts the hand-made pellets using epoxy resin as an adhesive. However, the pellets could not retain its shape when it was activated at high temperatures of 550 °C. It caused the pellet to lose the stability and it also burnt away by decomposition. But the pellets that were formed using sugarcane juice were able to retain the shape and structure of the pellet even after activation.

Figure 11, show the final activated pellet carbon that were formed using concentrated sugarcane juice as an adhesive for pellet formation. The activation was carried out at 550 °C in a tubular furnace with a retention time of 1 hour.

The pellet activated carbon was chemically activated using zinc chloride impregnation. The pellets were formed using concentrated sugarcane juice as an adhesive. The yield and iodine number of the pellet activated carbon that was formed by this procedure are present in Table 8.

Table 8 Yield Percentage and Iodine Number of pellet activated carbon produced.

Chemical Used	Impregnation Ratio	Yield (in %)	Iodine number (in mg/g)
Pellet Activated Carbon using Zinc Chloride ($ZnCl_2$)	1:1	36.9479	1100.7

The iodine number of the pellet activated carbon from table 8 is much more than the iodine number of other activated carbon produced chemically (from table 7). This points out that the pellet activation has acquired more activity compared to that of the powder activation, as powder activated carbon produced using zinc chloride has an iodine number of 1021 mg/g while pellet activated carbon produced using zinc chloride has an iodine number of 1110 mg/g. On a large scale production this surely has a greater effect.

Fig. 10. Hand-made pellets using epoxy resin as binder.

Fig. 11. Pellets made using concentrated sugarcane juice as binder.

4.6 CHNS Analysis

The ultimate analysis was done to get an idea about the elemental composition of the substances. The result of the ultimate analysis is shown in table 9.

Table 9 Ultimate or CHNS Analysis of coconut shell, powder activated carbons and pellet activated carbon.

Sample	Carbon (in %)	Hydrogen (in %)	Nitrogen (in %)	Sulphur (in %)	Oxygen (in %)
Coconut Shell Powder	48.09	6.012	0.00	0.017	45.881
Powder Activated Sample using Potassium Hydroxide (KOH)	68.00	2.383	0.00	0.004	29.613
Powder Activated Sample using Phosphoric Acid (H_3PO_4)	59.42	3.281	0.00	0.010	37.289
Powder Activated Sample using Zinc Chloride ($ZnCl_2$)	76.17	1.987	0.20	0.033	21.610
Pellet Activated Sample using Zinc Chloride ($ZnCl_2$)	74.51	1.321	0.56	0.013	23.596

The values from table 9, indicates that there is a steep rise in the carbon concentration on activation. This can be explained as the fixed carbon is the major component that is left over in addition to the volatile matter, ash and moisture content. All the four components are present as, in general a chemical reaction does not have 100 percent conversion rate. This could also explain the reason for the sharp fall in the hydrogen as well. But the value of nitrogen has increased in the zinc chloride activated samples. This is because the nitrogen gas which is used as the medium for activation is fixed on the surface or on the sample while activation. Hence there is a sudden occurrence of nitrogen concentration in the activated

carbons. Oxygen in the sample naturally gets used up during the analysis and it oxidizes other elements present in the sample. The highest amount of oxygen being present in the coconut really makes sense, as a large amount of oxygen in activated carbon is lost during the pyrolysis process.

4.7 Scanning Electron Microscope

The SEM was used to get proper images of samples at the microscopic level. These images are primarily used to determine the structure and distribution of the pores that are present on the surface of the activated carbon. It also determines the nature of the size of the pore, depending on the magnification of the image taken. The Scanning Electron Microscope images of powder activated carbon produced using potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) and pellet activated carbon produced using zinc chloride ($ZnCl_2$) are depicted in figure 12, figure 13, figure 14, and figure 15 respectively.

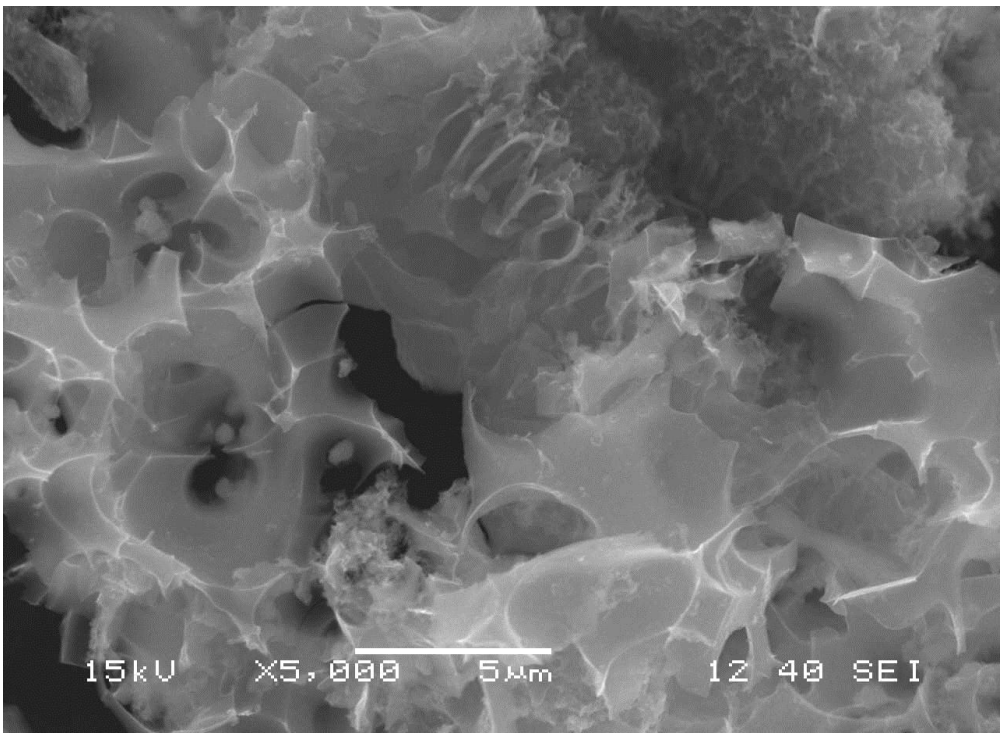

Fig. 12. SEM image of powder activated carbon using potassium hydroxide (KOH).

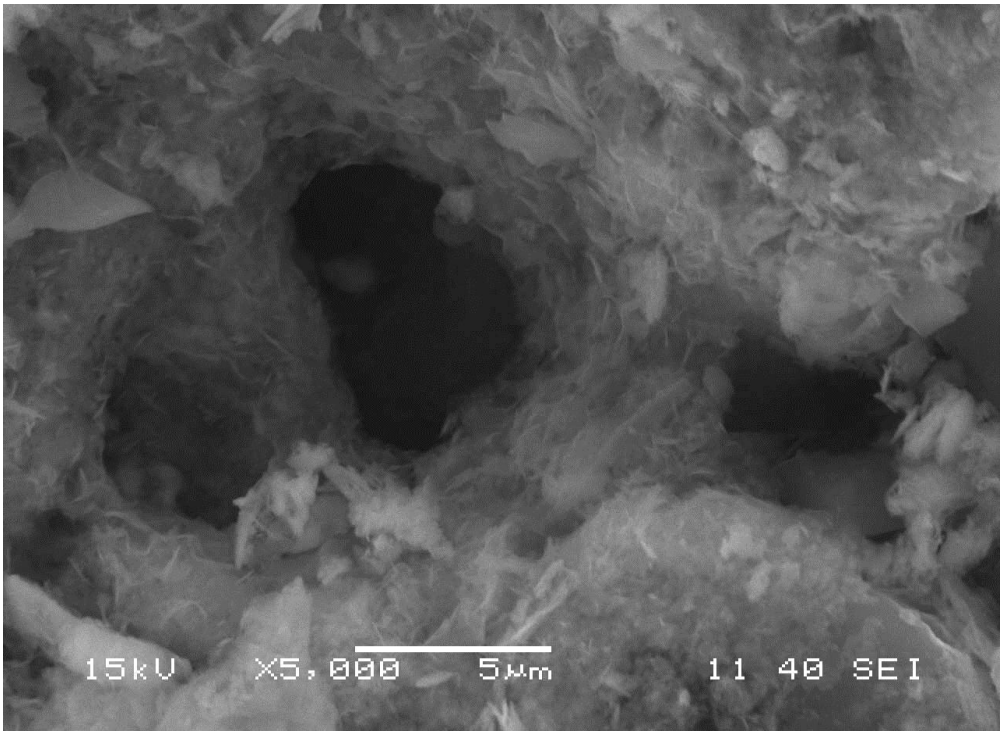

Fig. 13. SEM image of powder activated carbon using zinc chloride ($ZnCl_2$).

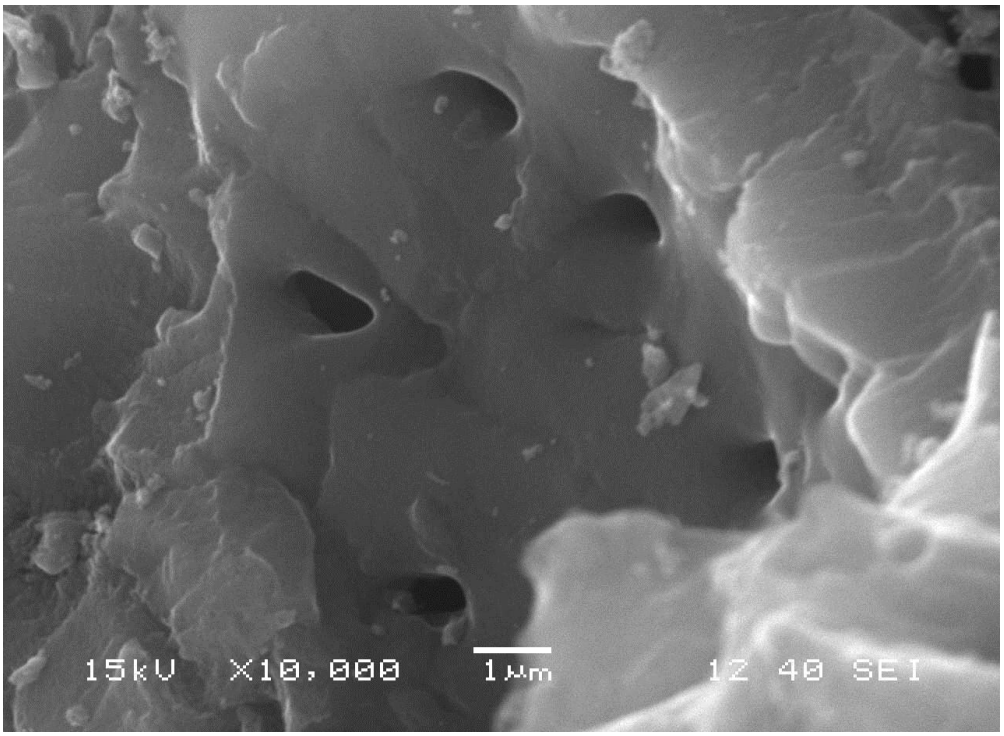

Fig. 14. SEM image of powder activated carbon using phosphoric acid (H_3PO_4).

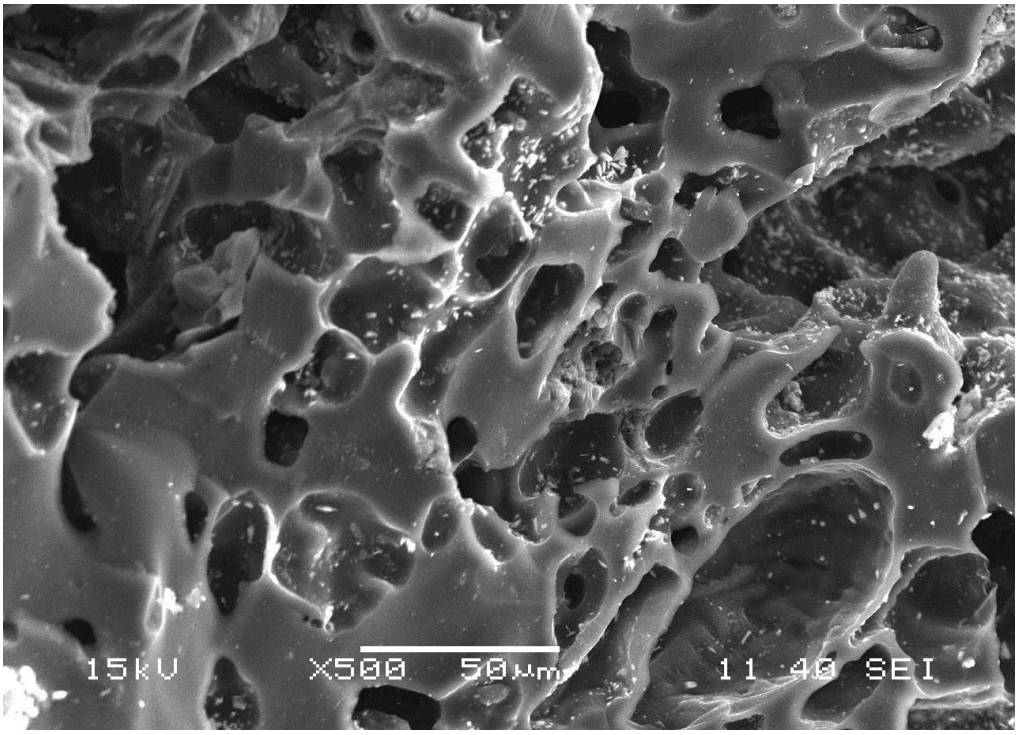

Fig. 15. SEM image of pellet activated carbon using zinc chloride ($ZnCl_2$).

From figure 15, it is evident that there are larger numbers of pores present in the pellet activated carbon produced using zinc chloride ($ZnCl_2$) activation than the other activated carbons. This supports the results of iodine number of pellet activated carbon being more than the other chemically activated samples.

4.8 Fourier Transform Infra-Red Spectroscopy

The FTIR Analysis result depicts the transmittance spectra of the powdered activated carbon, coconut shell and pellet activated carbon. From figure 16, coconut shell spectra's vibrations implies that it may have the presence of monomeric alcohols or phenols due to the wave numbers corresponding to 3618 cm^{-1}, 3520 cm^{-1}, 3296 cm^{-1}, 3270 cm^{-1}, and 3204 cm^{-1}. It also has peaks around the range of 1250 cm^{-1} to 1600 cm^{-1}, which might lead to the existence of alkanes, amines, nitro compounds and alkenes. Strong stretching vibrations at 1739 cm^{-1} may correspond to the C-H bonds of the Phenyl ring substitution overtones. The presence of N-H bonds of the amines and O-H bonds of the carboxylic acids are also suspected.

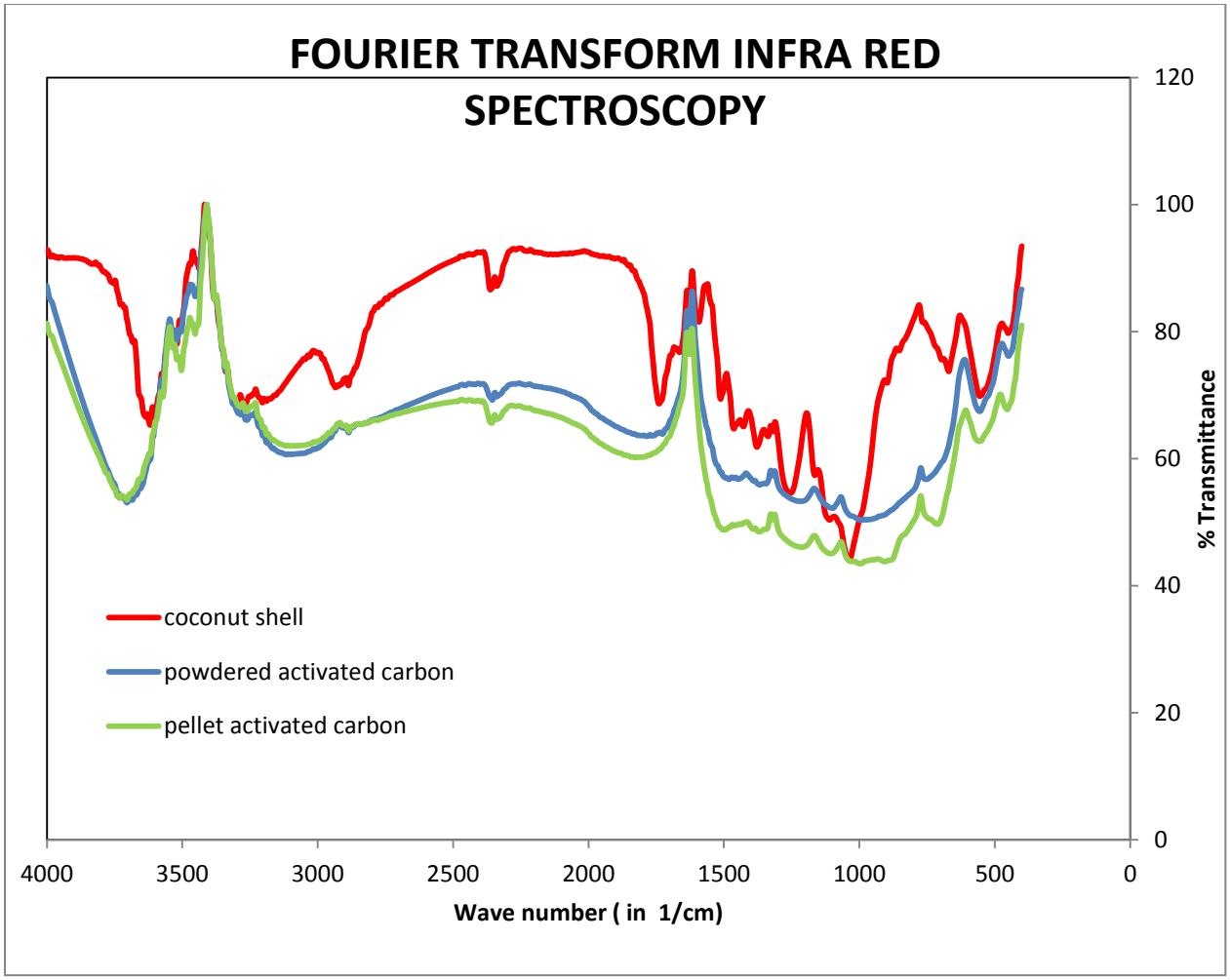

Fig. 16. Comparison of FTIR Analysis of Coconut shell, powder and pellet activated carbon.

However from figure 16, it can be observed that the spectra of the coconut shell and the activated carbon vary by large deviations. But the pellet and powder activated carbon spectra are almost the same, and might have few variations due to the presence of binders and excess nitrogen fixing on the surface.

The spectra of the powdered activated carbon have peaks at 1097 cm^{-1} which may indicate the existence of Alcohols, Ethers, Carboxylic Acids, and Esters. The vibrations are stretched from 2885 cm^{-1} to 3520 cm^{-1} thereby giving a clue for the presence of O-H bonds of carboxylic acids, monomeric alcohols and phenols, along with the presence of C-H bonds of aromatic rings and N-H of the amines. However the spectra of the Phenyl ring substitution

overtones are unchanged from that of the coconut shell spectra. Moreover, the spectra also imply a composition of alkanes, alkenes and CN amines present in the activated carbon.

The pellet activated carbon almost traces the same path as that of the powdered activated carbon, hence implying the composition of both these components might be the same almost. The few vibrations which deviate the spectra, might be mainly due to the presence of the excess aromatic rings, alkynes and phenyl ring substitution bands which have their vibrations at 1496 cm^{-1},3260 cm^{-1} and 710 cm^{-1} respectively.

4.9 Adsorption Studies

The adsorption studies were carried out in the setup as shown in figure 4. In the adsorption study Methane gas was used as the adsorbate. Methane gas was allowed to get adsorbed on the surface of the activated carbon at a varying pressure till 800 psi and a maximum temperature of 30 °C. Later the amount of gas adsorbed on the surface of the activated carbon was determined. The adsorption studies were done on a commercial activated carbon and pellet activated carbon that was prepared in the laboratory. The results of the adsorption studies are illustrated in figure 17.

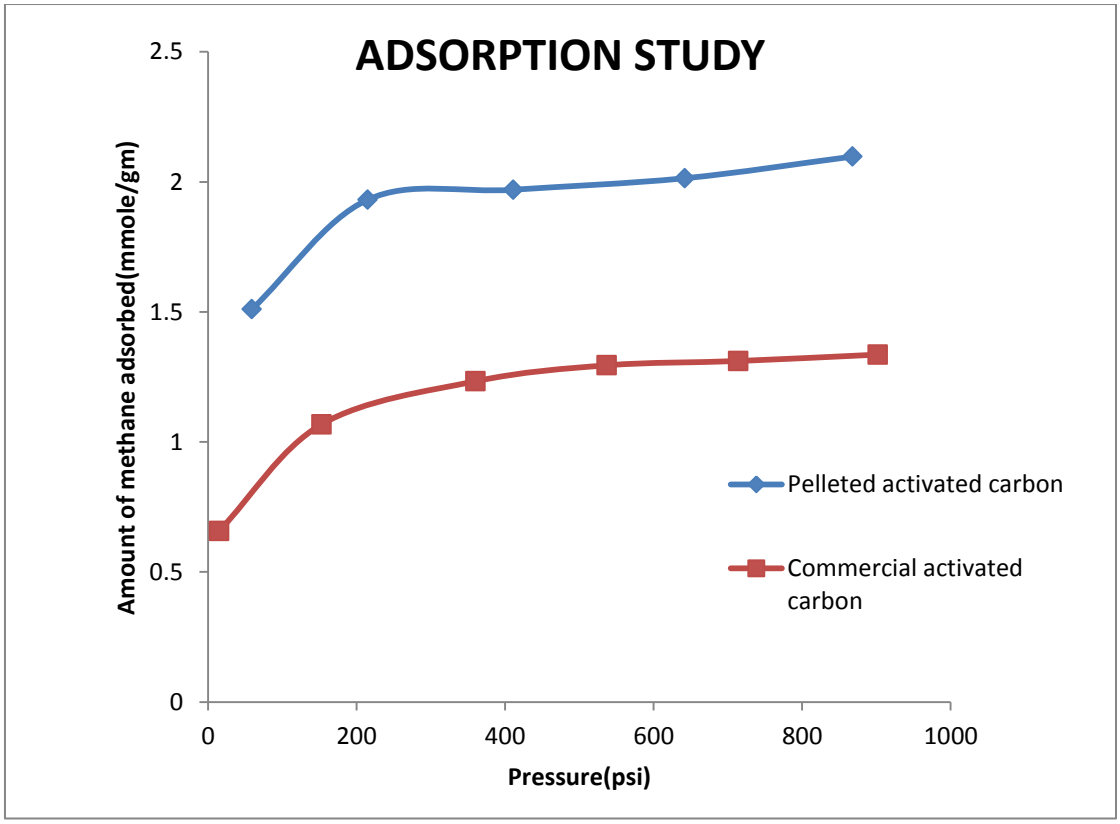

Fig. 17. Comparison of Adsorption Capacity of Pellet and Commercial Activated Carbon.

The plot shown in figure 17, clearly states that the amount of Methane gas adsorbed by the pellet activated carbon is much more than that of the commercially available activated carbon. This study gives a firm proof that large surface area are provided by the pellet activated carbon for adsorption. The pellet activated carbon high adsorption capacity due to high iodine number.

Chapter 5

Conclusion

5. CONCLUSION

The Thermogravimetric Analysis served as an initial guideline for determination of the exact temperature range in which the activation was to be carried out. With the help of these results, proper optimum retention time and temperature increments were used to determine the exact optimum temperature for the activation of coconut shell.

The proximate analysis of the coconut shell gave an insight of the nature of the precursor. Proximate results were very helpful in choosing the appropriate precursor. The quality of activated carbon is highly proportional to the dehydration rate of the sample and also on the process of removal of the volatile substances present in the precursor. According to proximate analysis, coconut shell has a volatile matter of 63% and moisture content of 9.5%. This contributes to a total volatile content (easily escapable components) of about 73%. Therefore, proximate analysis served as an evidence for choosing coconut shell as the precursor.

To determine the optimum temperature of activation, the coconut shell powder was activated from 500 °C to 620 °C. The yield percentage of all the activation experiments was recorded and noted. This yield were plotted to determine a suitable optimum temperature. But due to the fact that low yield experiments could also produce high active products, the idea of using yield percentage for optimization was dropped. Then the iodine number of the activated carbon was considered as a criterion for the determining the optimum temperature, as iodine number specifies the activity level (porosity level) of the substance.

Therefore, for identifying the optimum temperature, iodine number of various activated carbons was determined. Plotting a graph of these iodine number values against temperature, gave an optimum temperature of 550 °C with an iodine number of 119.39 mg/g. However, comparison of this value with the commercial grade activated carbons led us to the conclusion that only carbonization of the coconut shell has been done. Due to equipment inabilities, the physical activation using corrosive or oxidizing gases was not possible. Henceforth, the idea of physical activation of coconut shell was dropped and chemical activation was focused on.

Hand-made Pellets were formed using epoxy resin with a binder in specific ratio as an adhesive. The pellets formed were then activated in the furnace at 550 °C. But, upon activation, the resin melted away and decomposed. This made the pellets to lose its shape and structure. This test was a failure and gave an important inference of the resin not withstanding high temperatures. Therefore, the resin was not used as a binder for pellet formation.

Coconut shell powder was chemically activated using potassium hydroxide, zinc chloride, and phosphoric acid. The yield percentage of these chemically activated samples was considered for industrial and production significance. However to find out the porosity and adsorption activity of the samples, iodine number of these three activated carbon was considered. Based on the iodine number of these three activated samples, it was concluded that zinc chloride had the maximum activity. Henceforth zinc chloride activation of coconut shell powder was carried out.

As epoxy resin failed, concentrated sugarcane juice was used as a substitute for the preparation of pellet activated carbon. The pellets were made from the chemically impregnated samples. The pelletizer gun helped in producing uniform pellets with almost equal dimensions. The pellets were hardened on drying in the oven at 105 °C. Later these hard pellets were activated at 550 °C in a tubular furnace in nitrogen medium. Upon activation, the pellets did not lose its shape and structure. Hence the sugarcane juice served as an efficient binder for pellet formation. This confirmed that the sugarcane juice can be used as a binder for pellet formation and then can be activated at high temperatures without damaging the structure of the pellets formed. Large quantities of these pellets were prepared, washed, dried and stored for further studies.

The yield of the pellet activated carbon was also recorded. This does not have any significant impact on the small scale experimental procedure. But however is expected to have a great influence if the production is done in large industrial scales.

The iodine number of the pellets was tested. The result was very efficient and highest among all the activated carbon produced so far. This implied that the activity level of pellet activated carbon is much more enhanced than that of the powder activated carbon. It also concludes that the pellet formation using sugarcane juice has increased the characteristics or quality of the activated carbon. This could be thought as some synergistic effect of concentrated sugarcane juice along with the zinc chloride while activation. Increased iodine number surely has a direct impact on the pore size and pore density distribution.

The CHNS analysis also supports the view of pellet activated carbon being more enhanced than powdered activated carbon. From the results of the analysis, it is evident that the carbon percentage of coconut shell has increased with activation. The carbon percentage of pellet activated carbon is lower than its corresponding powder activated carbon using zinc chloride. This can happen only when excess carbon (present in the pellets) gets oxidized during the activation process on comparison with powder activated carbon. This leads to a greater loss in carbon percentage and also increases the pore volume and surface area. Hence, this accounts for the drop in carbon percentage and also for the high iodine number. The same analogy came be used to describe the drop in the other values namely sulphur and hydrogen percentage in the pellet activated carbon. Since there is a sharp increase in the nitrogen concentration, we can conclude that a part of the nitrogen flow is being fixed on the surface by the sugarcane juice or there is some concentration of nitrogen present in the sugarcane juice itself.

The Scanning Electron Microscope images gives fine details of the pores present on the surface of the activated carbon. From figure 15, it can be inferred that the pellet activated carbon has the largest pore-density distribution. The other chemically activated carbons (powder) may have lesser pore density than the pellets. This also supports and implies the idea of pellet activated carbon having a high iodine number.

The FTIR results give a rough idea about the composition of the precursor, powder activated carbon and the pellet activated carbon that is formed. It also helps to give an overview of the mechanism that is happening during activation. On comparing the CHNS and FTIR results we can conclude, that the initial precursor consists of a large amount of oxygen of can be considered as O-H groups. But however, after activation the presence of O-H bonds have

reduced, explaining that all the oxygen has been used up in the activation process, which tends to create porous structure on the substrate. The pellet activated carbon also has an increased presence of the nitrogen compounds spectra, due to the fixing of nitrogen on to its surface during activation or due to the presence of nitrogen in the sugarcane juice.

The adsorption studies performed on the pellet activated carbon and commercial activated carbon concluded that pellet activated carbon have more adsorbing capacity than commercial ones. It also specifies that for a low amount of surface area or low amount of sample a large volume of gas can be adsorbed. This helps in determining a useful application for the pellet activated carbon. From these studies, we may recommend this pellet activated carbon for the safe storage of Methane gas at high pressures. It may also be concluded that the pellet activated carbon is more active and must have high BET surface area than the commercial activated carbon.

The final conclusion would be that, highly active pellet activated carbon was prepared, developed and characterized from coconut shell powder as a precursor using sugarcane juice as a binder. It is also inferred that the sugarcane juice which served as a binder was cheap, natural and biodegradable, and high temperature resistant. This project was aimed at producing high quality pellet activated carbon by an economically cheaper method.

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